

1913  
M617

MILLER

Thiomesoxalate

Chemistry

M. S.

1913

UNIV. OF  
ILLINOIS  
LIBRARY

THE UNIVERSITY  
OF ILLINOIS  
LIBRARY

1913  
M617







THIOMESOXALATE

BY

ROLAND NORTON MILLER  
A. B. Lawrence College, 1911

---

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1913



1313  
11517

UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

June 5

190<sup>13</sup>

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Roland Norton Miller

ENTITLED

Thiomesoxalate

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

Master of Science

*C. G. Derick*

In Charge of Major Work

*W. A. Noyes*

Head of Department

Recommendation concurred in:

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

}

Committee

on

Final Examination





## THIOMESOXALATE.

### Introduction.

For some time a study of mesoxalic esters and their addition products has been carried on by Dr. R.S.Curtiss and his co-workers. Addition products with alcohols, amines, halogen acids, and other compounds having easily dissociable hydrogen atoms have been prepared, and in some cases intermediate addition products have been isolated.(1)

The study of these unstable intermediate addition products has lead to the explanation of a number of reactions that had not been explained satisfactorily before. Among these are the reactions of aldehydes and ketones with ammonia and substituted ammonias.

The study of the quantitative measure of polarity of ammonia and substituted ammonias as carried out by Dr.C.G.Derick at this University has lead to a satisfactory generalization that may be applied to predict the nature of the addition product that will form in the case of addition of ammonia and substituted ammonias to aldehydes and ketones.(2) This rule has been found to apply to the addition on the mesoxalic esters.

Additive reactions on the thioaldehydes and ketones have not been studied in the aliphatic series. To prepare and study the additive reactions on the thioketones Ethyl and Methyl mesoxalate in the light of previous knowledge of additive reactions on aldehydes and ketones was the purpose of this investigation.

A number of thioaldehydes and thioketones have been

(1)J.A.C.S.31-1053;33-400; and others. (2)Ibid.33-1162.

Digitized by the Internet Archive  
in 2014

<http://archive.org/details/thiomesoxalate00mill>



prepared, but it is interesting to note that the only monothio derivative in the aliphatic series is the monothioformaldehyde. The tendency of thioaldehydes and thioketones to polymerize accounts for the failure to prepare the monothio derivatives. It was hoped that the effect of the ester groups would be to prevent the polymerization in the case of thioesoxalates.

-HISTORICAL.-

Baumann and Fromm(1) prepared a tri-thioacetone by passing hydrogen sulfide into a mixture of equal parts of concentrated hydrochloric acid and acetone, immersed in a freezing mixture. The product diluted with water yielded an oily liquid of very unpleasant odor. This oil crystalized in a freezing mixture and yielded a product melting at  $24^{\circ}\text{C}$ . and boiling between  $225^{\circ}$  and  $230^{\circ}\text{C}$ . with partial decomposition. vapor density determinations showed a molecular weight corresponding to the formula,  $(\text{C}_3\text{H}_6\text{S})_3$ . Long heating at a temperature near the boiling point changed it to a di-thioketone of the formula  $(\text{C}_3\text{H}_6\text{S})_2$ . One of the reaction products of hydrogen sulphide on acetone was tetrathio-pentone, a crystalline body melting at  $171^{\circ}\text{C}$ .

Arno Behr(2) prepared what he thought was thiobenzophenon by the action of an alcoholic solution of potassium hydrosulfide on benzophenon. The product was crystalline and melted at  $152-3^{\circ}\text{C}$ .

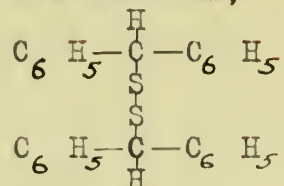
C.Engler (3) asserts however that this product which he obtained by the action of ammonium sulfide on

(1) Ber. 22-1035. (2) Ber. 5-970. (3) Ber. 11-922.





benzophenon is of the formula,



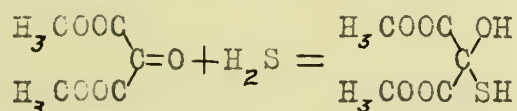
rather than  $\text{C}_6 \text{H}_5 - \overset{\text{S}}{\text{C}} - \text{C}_6 \text{H}_5$  as Behr asserts. The compound  $\text{C}_6 \text{H}_5 - \overset{\text{S}}{\text{C}} - \text{C}_6 \text{H}_5$  Engler prepared by the action of potassium sulphide on benzophenon and found that it melted at  $146.5^\circ\text{C}$ . Behr's compound he prepared by the action of potassium sulfide on benzhydrol chloride.

Engler(1) also prepared thioacetophenon by a reaction analogous to that which yielded thiobenzophenon.

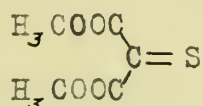
C. Wilberoth(2) prepared a di-thioacetone by the action of freshly prepared yellow ammonium sulfide on acetone. His product melted at  $183-85^\circ\text{C}$ . and is the same that Baumann and Fromm prepared by heating tri-thioacetone.

#### -RESULTS AND DISCUSSION.-

In accordance with the action of water, amines, alcohols and other compounds having easily dissociable hydrogen atoms, on mesoxalic esters, it was expected that hydrogen sulfide would add on thus:



Upon dehydration this should yield:



The action was slow however, twentyfive minutes passing

(1) Ber. 11-930. (2) Ber. 20-2467.

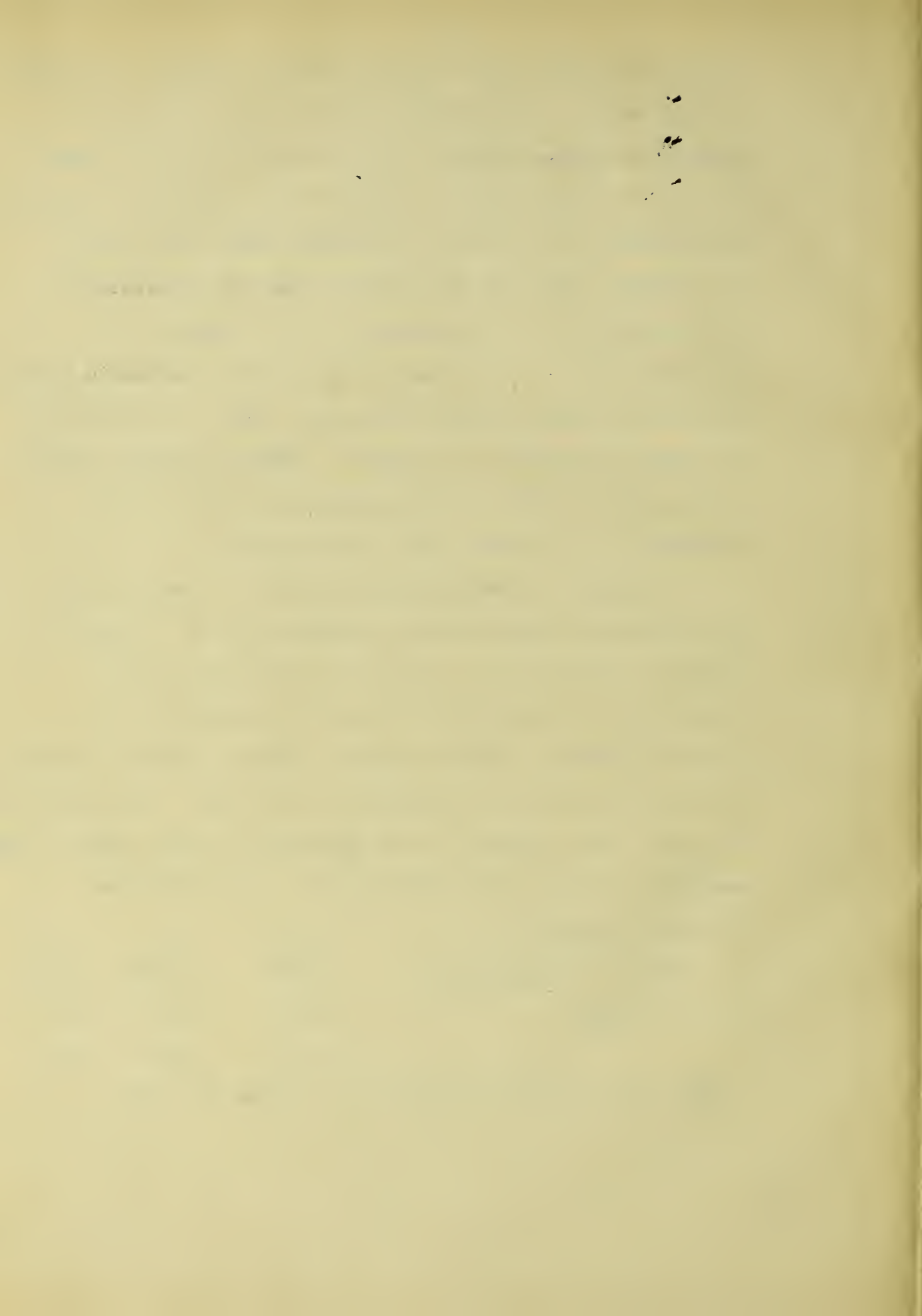


before any change other than a slight increase in temperature of the ketone through which the hydrogen sulfide was passing could be noticed. The product crystallized from ether was a white sandy crystalline body melting at  $102.5-3^{\circ}$  (uncorrected). The product decomposed when heated above its melting point and the ketone ester was regenerated. This behavior is in accordance with the behavior of addition products previously obtained with mesoxalic esters, and is sufficient grounds for saying that the product in this case is an addition product. This is further shown by the loss of color of the ketone ester due to the breaking of the double bond to the oxygen.

Attempts to dehydrate the product by heating for four hours with phosphorus pentoxide failed. Acetyl chloride dissolved the substance on heating without evolution of hydrogen chloride or the formation of a reaction product. Metallic sodium reacted extremely slowly on a solution of the substance in dry ether. The action in this case was on water in the imperfectly dried ether. The analysis of the product corresponds to the empirical formula:  $C_{10}H_{14}O_{10}S$ .

	C	H	S
Theory for $C_{10}H_{14}O_{10}S$	36.8%	4.29%	9.81%
Found	I 36.64	4.25	9.77
	II 36.92	4.42	9.93

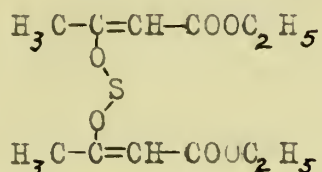
These facts point to formula "A" rather than "B".







The peculiar oxygen-sulfur linking is not without precedent. A. Delisle(1) prepared a compound by the action of sulfur di-chloride on acetoacetic ester and assigned to it the formula:



The same linking is also found in ethyl or methyl sulfuric acid.

The addition however is contrary to the usual process of addition to the mesoxalic esters.

Phosphorous pentasulfide was found to react violently with the ketone ester when heated to 135-40°C., producing a quantity of foul smelling vapors. Upon dissolving the ketone in sodium-dry xylene, the action proceeded quietly and produced a quantity of red sticky gum. Attempts to crystalize this failed. Upon distilling it decomposed and yielded a dark brown, sticky carbonaceous mass and a brown liquid smelling like garlic. The substance causing this odor was not obtained in sufficient quantity to purify and analyse.

Action between di-bromo malonic esters and potassium sulfide was brought about by passing the vapors of the ester over potassium sulfide ground to the size of wheat

(1) Ber. 22-306.



and contained in a tube heated in an air bath to 200°C. The action was carried on under reduced pressure. The product was a mixture of di-bromo ester and a small quantity of a substance having the same garlic odor as was noticed in the vapors formed in the decomposition of the product formed by the action of phosphorous pentasulfide on the ketone ester.

#### EXPERIMENTAL.

##### Action of Hydrogen Sulfide on Methyl Mesoxalate.

Hydrogen sulfide was passed through thirteen grams of ketone contained in a glass tube. After eleven minutes there was a slight increase in the temperature of the tube. After twenty minutes there was a loss of color of the ketone ester. At the end of twentyfive minutes a few small crystals formed and increased rapidly in number until at the end of one and one half hours the contents of the tube was a pasty mass. Cooling in an ice mixture did not increase the rate of precipitation. The contents of the tube was removed and spread on the bottom of an Erlenmeyer flask and the gas passed through for four hours more. At the end of that time the contents of the tube was dry.

##### Properties of the Product.

The product recrystallized from ether was white and finely crystalline. It was easily soluble in xylene; fairly soluble in chloroform; easily soluble in acetone; fairly soluble in carbontetrachloride; fairly soluble in cold benzene; fairly soluble in hot ether. It was difficultly soluble in cold ether cold xylene and cold ligroin. It was





soluble in water with liberation of hydrogen sulfide. The water solution yielded di-hydroxy malonate, the product of the action of water on the mesoxalic ester. The substance melted at  $102.5-3^{\circ}\text{C}$ .

#### Action of Phosphorous Pentasulfide on Methyl Ester.

Five grams of ketone, four grams of phosphorous pentasulfide and an equal volume of sodium-dry xylene were heated in a small flask closed with a calcium chloride tube. The heating was carried out as near  $135^{\circ}\text{C}$ . as possible in an oil bath. The action began at once and the contents of the tube turned red rapidly. After heating for one and one half hours the action was completed. The tube was removed from the bath and the contents extracted with ether. The extract was distilled until all the ether and xylene was removed and the residue was then taken up with ether. The solution was evaporated in a vacuum dessicator.

#### Properties of the Product.

The residue after evaporating the ether was a thick red gum with a penetrating odor. Cooling to  $-10^{\circ}\text{C}$ . hardened it to a waxy consistency but crystallization could not be induced. The substance was soluble in ether, benzene, and ligroin but insoluble in water. Upon distilling it decomposed.

#### Action of Di-bromomalonic Esters with Potassium Sulfide.

The di-bromoester was distilled into a tube containing potassium sulfide ground to the size of a grain of wheat. The tube was heated to  $200^{\circ}\text{C}$ . by means of an air bath. The action was carried out at 22-25 mm. pressure. The distillate was a mixture of di-bromoester and a small quantity of an oily



liquid. This liquid had an intensely garlic odor and caused copious tears when the vapors came in contact with the eyes. It was not obtained in sufficient quantity to purify and analyse.

I desire to express my thanks to Dr. Richard S. Curtiss under whose direction and with whose assistance this investigation was carried out, and also to Dr. C. G. Derick for his assistance in preparing this thesis.











UNIVERSITY OF ILLINOIS-URBANA



3 0112 086859128